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KINETIC METHOD BY USING CALORIMETRY TO MECHANISM OF EPOXY–AMINE CURE REACTION

IV. Thermochemistry of the epoxy–amine curing at the later stages of the reaction

R. M. Vinnik[1] *and V. A. Roznyatovsky*[2*]

[1]N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Kosygina str. 4, Moscow 117334, Russia
[2]Chemistry Department, Moscow State University, Moscow 119899, GSP-3, Russia

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Abstract

Some specific features of the thermochemistry of epoxy–amine curing at the later stages of the reaction are considered. Possible mechanism of cross-linking and the question about the driving force leading to the infinite network are discussed. The coupling of the reaction kinetics and rearrangement of the chains crosslinked into the rigid supramolecular structure is the essential feature of epoxy–amine vitrified system. It has been proposed that owing to the contribution from the side process, different curing temperatures can result in the structures with different T_g. It was also established that reaction of epoxy ring opening alone is not responsible for the residual curing. The latter is the result of the side processes. As compared with the reaction of epoxy ring opening the side processes are strongly dependent on the geometrical aspects.

Keywords: cure reaction, DSC, epoxy–amine, vitrification

Introduction

This paper is another in series of publications on the thermochemical study to the epoxy–amine cure reaction. Previous papers of this series reported the results of using the calorimetric method to the kinetic study [1–3].

The kinetic analysis of the epoxy–amine cure reaction by using calorimetry is a field as not simple as that of glass state problem itself. The principal difficulty does not lie in obtaining the experimental curves, but in obtaining the conversion rate dependencies.

We looked again to thermochemical kinetics to offer another approach. In preceding studies [1–3], our work was built up on purely kinetic consideration has demonstrated that kinetic analysis may be successfully carried out without complicated mathematical apparatus.

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[*] Author for correspondence: E-mail: vit.rozn@chem.msu.ru

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Using Mangelsdorf's method, however, allows both kinetically based separation of the heat effects and detecting of the concurrent processes. The existence of these heat effects in epoxy–amine curing reactions have not been observed previously. This is probably due to the fact that traditional method of kinetic analyses does not allow to separate concurrent processes.

The model, which is normally used today to describe the process of formation a rigid network of glass state system, is based on the diffusion type of process. Nearly all of the cure kinetics has been interpreted in terms of a mechanism involving the reactant diffusion and levelling off. This is the standard comment and description of cure reactions found by the authors of this study in all papers they had in hand. Since extensive motion within a relatively rigid matrix is always a difficult problem, the attractiveness of such a hypothesis is readily apparent. This is especially true in the case of solid-state polymerizations, where many small molecules must join to form a single large one.

This phenomenon appears to be fairly clear in radical polymerization [4, 5] and not too surprising that in the case of epoxy–amine reactions this picture has at times been inferred simply on the ground that curing process takes place in the solid state [6, 7]. However, in the case of the reaction between diepoxy- and diamine-molecules, this reasoning is naive inasmuch as with liquids such as epoxy–amine mixture we have a much different situation. The kinetic analysis shows that there is no indication of any realization of the mechanism involving the reactant diffusion when applied to the epoxy–amine cure reactions [1–3]. The low degree of conversion in the late stage of epoxy–amine cure reaction, for example, may be satisfactorily explained by miscalculation of the degree of conversions [8].

The usual concept that the rate of a chemical reaction is directly related to the probability of diffusion of the reacting species takes no account of the effect of the medium composition on the kinetics of chemical interactions. It has recently become usual to allow for the effect of the medium on the kinetics of liquid-phase reaction [9]. However, there are certain reactions whose mechanisms are hard to examine, because no solvent is present in an explicit form. Among these reactions is formation of amine-cured epoxide to yield a thermally stable polymer.

It is important to emphasize that there is much evidence to support the view that the solvent-free systems termed solid-state reactions are oversimplified. For example, the possibility of solid-phase organic reactions is considered in [10] where these reactions are reported to afford high conversions.

In order to substantiate the kinetic model [1], it is useful to consider other evidence present in literature. As is well known, the kinetic features of the reactions in frozen solvents have long been established and the studies of reactions in frozen organic solvents and in water are well documented [11–14]. Much can be learned from these literature of the 1970's which contributed to the understanding of the reactions in frozen solvents. Here, the above-mentioned reactions were completely explained by reaction only in liquid regions of the frozen system. Thus, in study of the acid- and base-catalyzed hydrolysis of acetic anhydride in water and in ice have been presented evidence that in frozen solutions the reaction components are gathered together in regions which remain liquid [13, 14]. The liquid regions are necessary for reaction progress; no controlled reactions involving the total solid phase have been reported. Other striking effect was also observed [11], namely, the freezing of aqueous solutions caused a change in kinetic order and the kinetics became first-order behavior.

There is clear trend that epoxy-amine reaction rate increases with increasing in amine component. Here the clear catalytic action exhibited by excess amine come from the kinetic data, suggesting the presence of the initial association between reagents during the cure reaction [2]. Non-covalent interaction between the reagents hold the functional groups in a conformation that favours reaction in >90% yields. To be precise, the data obtained by titrimetric analysis furnish the conversions nearly to 98%. References may be made to [15–19].

Such associated reaction medium can be regarded as a logical first step toward engineering more complicated three-dimensional assemblies with well-defined architectures. The existence of association between epoxy and amine molecules is prerequisite for reaction in these systems.

In Eq. (1) an extension of the Horie model [20] to include the association between reagents was set forth to calculate the reaction kinetics. We derived the kinetic Eq. (1) in the terms of the heat release rate by using Mangelsdorf's method [21]:

$$\begin{aligned} W=&Q_{\mathrm{mol1}}k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})+Q_{\mathrm{mol2}}k_{\mathrm{ef2}}(C_0-C_{\mathrm{x}})(C_{\mathrm{x}}-C_{\mathrm{x3}})+\\ &+Q_{\mathrm{mol3}}k_{\mathrm{ef3}}[(C_{\mathrm{x}}-C_{\mathrm{x}}^{\mathrm{sat}})-C_{\mathrm{x3}}](C_{\mathrm{x}}-C_{\mathrm{x}}^{\mathrm{sat}}) \end{aligned} \tag{1}$$

where C_{x} is the total concentration of OH groups for both reactions: uncatalysed and autocatalysed; C_{E} is the initial concentration of functional groups of epoxy resin in mol L^{-1}; C_{A} is the initial concentration of amine groups in mol L^{-1}, C_0 is the initial concentration of the deficient reagent, $k_{\mathrm{ef1}}$and k_{ef2} is a rate constant for reaction of epoxy ring opening.

The second term in Eq. (1) involves the concentration of the complex (C_0–C_{x}) in mol L^{-1} consisted of the molecules amine and epoxide. The subscript $_1$ and $_2$ identifies a contribution of the heat of epoxy ring opening (kJ mol^{-1}) in 'uncatalyzed' and autocatalyzed reactions, respectively, and the subscript $_3$ refers to the later stages of the reaction where the reaction is accompanied by diffusion of the reaction products. At that, we allow the coupling between the reaction and the collective mobility of the particles composing the solid matrix.

The last term involving the diffusion of the reaction products is included here to extend the kinetic model to the case of the interaction under vitrification. Following the Two-Fluid scenario proposed by Bendler and Shlesinger [22], which believe the explanation of glass structure formation lies in the splitting of the homogeneous mixture into two liquid phases, we formulated the last term in Eq. (1) as a saturation with OH groups reacting medium. By this is meant that the newly formed OH groups leave the reaction medium.

The main problem associated with finding the correct explanation for the rate enhancement at the late stages is that details of the splitting of the homogeneous mixture into two liquid phases during the vitrification are not known. Some interesting features were found in [23], but their detailed analysis at the late stages has not fully been developed because of a lack of data on the mechanism of the infinite network formation as well as data on DSC scans of cured polymer under study. Following our previous studies that considered thermokinetics and the cure mechanism of epoxy–amine system [2, 3], in this paper, we report data on DSC heating scan of cured polymers. Moreover, the present paper is an attempt to combine the data available in the literature with our findings on calorimetry of amine cured epoxide system.

Experimental

The data of the present study have been combined with those from previous investigations [2, 3] in which under isothermal conditions, the cure kinetics was measured embracing effects of reactant concentrations and temperature.

Samples were prepared as previously described [2, 3]. Calorimetric data were obtained by using differential scanning calorimeter DSC-111 (‘Setaram’, France) as well as isothermal calorimeter DAC-1-1 (Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka). About 0.3 g of a sample was placed in instrument at the desired temperature for the desired period, during which the heat evolved during reaction was continuously measured. After the isothermal curing, the samples were annealed and a dynamical run was conducted at heating rate of 5ºC min^{-1}. All DSC runs were carried out at heating rate of 5ºC min^{-1}. Each material was run twice and the glass transition temperature T_g was measured on all the samples where T_g was measured at the onset of the glass transition region.

Results and discussion

Figure 1a shows the DSC heating scan of cured polymers after annealing at 23ºC. The characteristic revealed in these DSC scans is the presence of two distinct exothermic peaks with peak temperature 120 and 230ºC.

One of these peaks is most likely to be contributed by the heat generated via etherification reaction. It is well known that the etherification reaction is only observed for the mixtures with an excess of epoxy [24–27]. Moreover, it is shown that at excess of epoxide intramolecular etherification may be the main reaction [28].

Figure 1b shows the sample, which has been cured in a large excess of epoxy at 50ºC, conditions under which the etherification reaction can take place during the reaction. Curves of this figure represent the first and the second scans of the samples when the epoxy is taken in excess over amine. The line (1) is the first scan, and the line (2) represents the second scan taking right after cooling from the initial one. As is clearly seen, presence only one peak with peak temperature 230ºC is evident. In the composition with a large excess of epoxy, as is apparent from this figure, the contribution of this reaction increases significantly with increase in the epoxy content. Early investigations made on the cured samples with an excess of epoxy, found the reaction between an excess of epoxy and OH-groups [29]. At that, the data obtained by IR spectroscopy furnished the fully reacted amine.

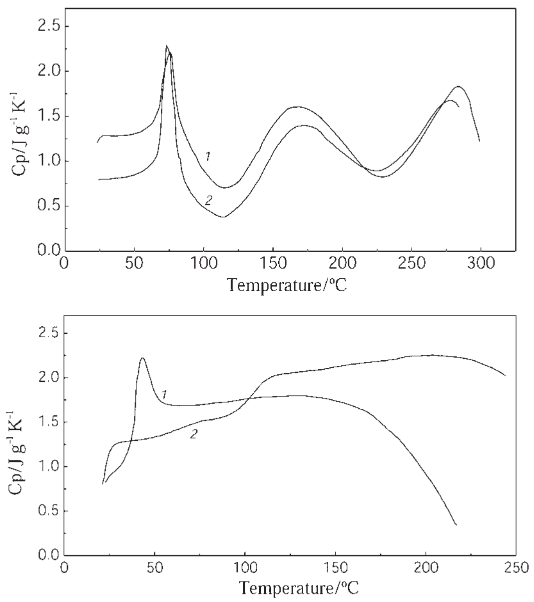

Fig. 1 DSC heating scans of cured polymers after annealing at 23°C: the ratio of functional groups amine/epoxy equals: a – 1–0.8; 2–0.9; b – 1–0.6 (the first scan); 2–0.6 (the second scan)

Figure 2 shows that the exothermic peak, but in contrast to formulations with an excess of epoxy, with peak temperature in the range of 80–100ºC, occurs during the scans of the samples when the amine is taken in excess over epoxide. Comparison of these heat effects shows that their magnitude as well as peak temperatures is directly dependent on the amine excess.

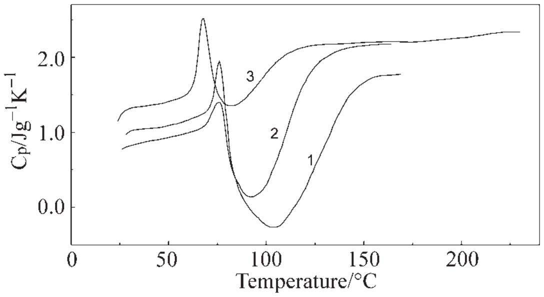

Fig. 2 DSC heating scans of cured polymers after annealing at 23°C: the ratio of functional groups amine/epoxy equals: 1–1.2; 2–1.6; 3–1.9

We have analyzed, according to Eq. (1) thermokinetic curves for the reaction under study [1]. In the course of our study of epoxy–amine kinetics in which cure isotherms were obtained employing stoichiometric quantities of diamine, we have paid special attention to the fact that the endothermic process was most observed in curing

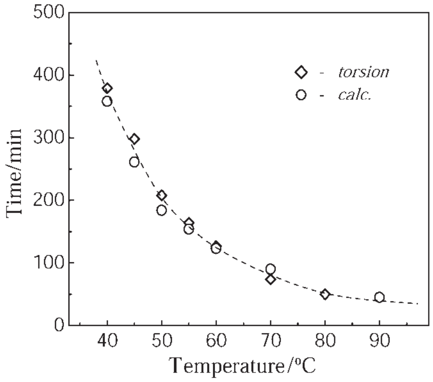

Fig. 3 The results of the torsional braid analysis (rhomb). The data determined from the calorimetric measurements (circle)

reaction in the range from 40 to 55°C; the endothermic effect was discovered in examining the kinetic curves. In other cases, this effect was smallish. To illustrate the reliability of the data obtained by the calorimetric method, Fig. 3 shows the results of the torsional braid analysis together with the data determined from the calorimetric measurements [3]. As is shown in Fig. 3, the results of these methods are found to be in fairly good agreement. Meanwhile the temperature dependence of Q_{mol3} obtained from the isothermal kinetic experiments shows that endothermic heat is dependent on the curing temperature [3]. Inspection of Fig. 2 in [3] shows that Q_{mol3} decreases significantly with the increase the cure temperature.

The variations in Q_{mol3} obtained during the cure reaction for formulations with excess of amine are given in Fig. 4. As judged from the Q_{mol3} values, in this case the endothermic heat decreases as the composition approaches to stoichiometric proportion. We explained the endothermic process as the transfer of the new formed OH groups to solid matrix [1–3]. Therefore, we assume that the endothermic effect occurs in combination with rearrangement of the chains crosslinked into the rigid supramolecular structure. Then the endothermic effect must be most observed in stoichiometric composition.

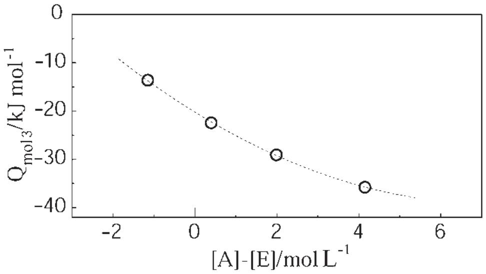

Fig. 4 Variation of Q_{mol3} as a function of the reagent ratios for formulations with excess of amine; curing temperature 50°C

The observed variation in Q_{mol3} can be explained by the competition between endothermic and a side exothermic processes that masks part of the endothermic heat during the cure reaction. At that in comparison with the endothermic effect, the magnitude of a side exothermic process is sufficiently great both at high curing temperatures and in stoichiometric formulation. To quantitatively compare the kinetic calculation with the data obtained by the heating DSC scans from the area under the DSC curves, we determined the residual heat evolved after isothermal experiments. Figure 5 represents plots of the degree of conversion *vs*. the composition for amine-rich cured samples calculated from kinetic curves and the results obtained with DSC scans. As can be seen, except for stoichiometric compositions where a lower degree of conversion was observed for the data obtained by kinetics the approximation between the calculation and the experimental results is very close. At that, the result of the titrimetric analysis marked filled circle falls in almost the same plot of the degree of conversion *vs.* the composition. Since the conversions in the latter are lower than required by the heating scan experiments, it is possible that as the composition approaches to stoichiometric proportion additional process come into play at the last stages of the reaction.

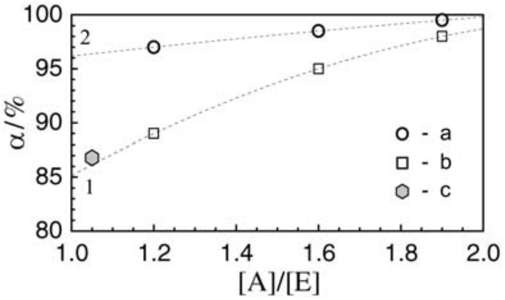

Fig. 5 Plots of the degree of conversion *vs.* the composition for amine-rich cured samples: 1 – data calculated from kinetic curves, 2 – the results obtained with DSC scans

It should be noted that exothermic peak was not seen along the first scan of the annealed sample cured at 100ºC. As is shown in Fig. 6 (first line), this sample demonstrated typical DSC scans of epoxy series [30, 31]. The second curve in Fig. 6 represent the second scan taken right after rapid cooling from the initial one. The data further in Fig. 6 strengthen the conclusion that the absence of the endothermic effect during the reaction at 100ºC is the result of the competition between endothermic and a side exothermic processes.

Nevertheless, the origin of this exothermic effect is still unclear. Generally, accepted explanation the exothermic peak appeared in the heating scans is like residual curing. The simple basis of argument in favour of the residual curing is that literature contains compelling evidence that glass transition temperature of the cured system depends on cure temperature. As is well known, formation of cured polymer is accompanied by a considerable rise in the T_g of the reacting system [32]. Moreover, it is

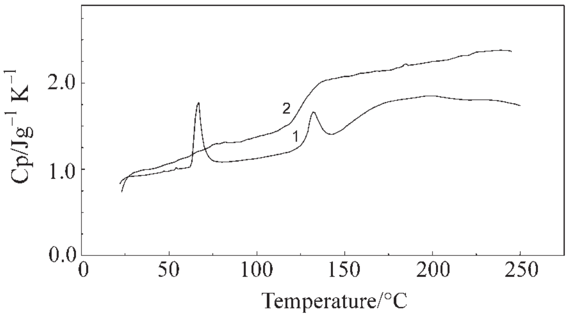

Fig. 6 DSC scans of the sample cured at 100°C. 1 – the first run, 2 – the second run

well known that the relationship between T_{cure} and T_{g} is a most outstanding characteristic of the amine cured epoxy system [33].

The results in Fig. 6 provide evidence that the concept of the residual reaction of the epoxy-ring opening is not verified in the case of higher cure temperature such as 100°C ($T_{\mathrm{cure}}<T_{\mathrm{g}}$). Different curing temperatures are supposed to result in the structures with different T_{g} owing to the contribution from the side processes.

These experimental results may be fully explained if we will analyze the literature data.

Since none of the infinitely large skeletal networks has been isolated and no physical evidence of their occurrence exists [34] the epoxy–amine cure reactions must be relative to a field of supramolecular chemistry [35, 36]. In [36], a concept based on self-organization was demonstrated by the example of thermally cross-linked nanostructured phenolic resins.

A curiously unanswered question about the curing reaction is the driving force of the infinite network formation. It must be admitted that the truth is that the kinetic model developed in [1] does not suggest clear-cut answer to the question of the mechanism of high cross-linked structure formation.

Our present results are understood well if we will assume that solvophobic interactions participate in the mechanism of high cross-linked structure formation.

Available literature [37] data provide the support that this interpretation could be valid. It is well known that in certain composition regions the hydrophobic interaction play an important role in the glass-forming behavior of some inorganic salt aqueous and alcoholic solutions [38–40]. We are not, of course, suggesting that what follows is an accurate portrayal of the situation in aqueous and alcoholic solutions; however, certain features of the epoxy–amine system, namely, hydrogen-bonded network are indicative of those in aqueous solution.

Thus, if solvophobic interactions provide the foundation for association of networks into infinite network, it is reasonable to assume that the formation of the infinitive network during the cure reaction is indeed consistent with a solvent (low-molecular mass liquid) – induced aggregation of network molecules into a giant three-dimensional network due to the solvophobic effect. By solvent is meant the low-molecular mass liquid. To be precise, the dominant mechanism by which the polymer molecules affect this process is through its effect on the structure of low-molecular mass liquid [41]. In our view, the vitrification of the associated reaction mixture can have solvophobic character. Namely, solvophobic interactions are believed to be closely related to incorporating microgel particles into polymolecular assembly and to contribute to the maintenance of infinite three-dimensional network, since dissolving polymer molecules containing hydroxyl groups has a structure-promoting effect. A hydroxyl group has a supramolecular valence of two, corresponding to a pair hydrogen bonds one donated and the other accepted. This interpretation would reasonable be expected to explain the fact of the self-assembly into the infinite three-dimensional structure. In other words, the formation of infinite three-dimensional network is considered to be physical gelation and not covalent crosslinking.

So far, the published chemistry of amine cured epoxide reaction describes the interactions of functional groups: amine and epoxy. In the published chemistry of amine cured epoxide reactions, a detail understanding of the rate controlling mechanism is still restricted to model reactions. Notably, the author [42] would have us believe that chemistry exhibited by the curing processes is identical to model reactions, which are investigated well.

Nevertheless, as follow from the thermochemistry of the process under consideration, indeed more work along this line is needed. For example, the residual curing can involve, in addition to the opening of the epoxide ring by reaction with hydroxyl groups, the interaction between OH-groups [43].

According to our scenario where the polymer molecules are built up by polycondensation, but are networked by solvophobic interactions and hardened for the most part by side processes, the thermochemistry of the reactant system as a whole involves the heat effects of the processes: reaction of epoxy ring opening by amine, diffusion of the reaction products into the solid matrix and side processes. Also, the structure of macromolecules, to our knowledge, can be stabilized by long lived hydrogen bonds, in other words, the strong H-bonds [44]. For the strong H-bonding between hydroxyl groups occurs there must be a significant amount of hydrogen-bonded hydroxyl groups. Apparently, strong H-bonding between hydroxyl groups as well as the covalent interaction between the hydrogen-bonded hydroxyl groups depends on the geometric arrangement of reactive groups. Therefore, except the etherification reactions, side processes can be H-bonding between hydroxyl groups, which interchain neighboring OH groups in a given system of reactants [45].

In view of supramolecular concept [35], the reaction of epoxy ring opening by amine generates mainly ‘building blocks’. Therefore, construction of the supramolecular system is not directly determined by the structure of the single ‘building block’ but the structure formed by aggregation of the latter. Thus, the cured polymer may be viewed as structure with network molecules acting as ‘building blocks’ and above mentioned interactions serving as their connections. The behavior of the vitrified system is directly related to the stability of these crosslinked ‘building blocks’ acting as junction points in the network. More precisely, due to side processes the supramolecular system become thermostable. Until now, there is no conclusive answer to the origin of this side processes and more research work has to be done in this area in the future.

Conclusions

The results of kinetic treatment clearly indicate that additional to the exothermic epoxy ring opening by amine occurs another exothermic reaction, which completed during the DSC heating scan.

The Mangelsdorf's approach used here provided an important step toward using calorimetry to mechanism of amine cured epoxy polymer formation since this method allowed the treatment of the kinetic curve even in the last degree of conversions and to elucidate the evolution of the vitrified polymer structure from reaction of epoxy ring opening by amine. In view of the kinetic features of this reaction [1–3], generally accepted explanation like residual curing by reason of the levelling off of the degree of conversion at advanced stages of the reaction of epoxy ring opening by amine, seems very unlikely.

As a provisional hypothesis, we proposed that in vitrified system, for the most part, the appearance of the side processes is responsible for the residual heat evolved during the heating scan. Thus, the thermochemistry of the reactant system as a whole involves the heat effects of the processes: reaction of epoxy ring opening by amine, diffusion of the reaction products into the solid matrix and side processes.

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